Removal of Chromium (VI) from aqueous solution using surfactant impregnated activated carbon

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Abstract— **Adsorption process using Surfactant Impregnated Activated Carbon (SIAC) was studied to remove chromium (VI) from aqueous solution. Objective of this study was to investigate the effect of anionic surfactant on the adsorption of hexavalent chromium onto activated carbon by using Sodium Lauryl Sulfoacetate (SLSA) as surfactant. Different surfactant concentrations impregnated onto the activated carbon was studied on the removal of hexavalent chromium in aqueous solution. Based on the result of this study, it shows that the removal of Cr(VI) using Surfactant Impregnated Activated Carbon (SIAC) decreases as concentration of surfactant increases due to the electrostatic repulsion of hexavalent chromium that exists as dichromate ($Cr_2O_7^{2-}$) ions with the surface functional group of SIAC.**

***Keywords*— Sodium Lauryl Sulfoacetate (SLSA), Surfactant Impregnated Activated Carbon (SIAC), Hexavalent Chromium.**

I. INTRODUCTION

Water is widely used in industry and also important to all forms of life. Nowadays, there are many cases of water pollution due to the presence of substances or conditions that makes the water not suitable for specific purposes. Industrial wastes, agricultural wastes, human daily activities and also transportation contributed to water pollution.

Electroplating industry is one of the sources that caused large amount of heavy metals discharged through wastewater. This is because electroplating is a plating process which metal ion are used to coat and electrode by an electric field. This process can improve the characteristics of a surface and also product appearance. There are many industries that involve in this electroplating process such as automobile, electronics and jewelry. Besides, there are other industrial processes that generate liquid wastes containing toxic heavy metals such as chemical manufacturing and also in coal and ore mining. Coating process uses various types of metal include chromium (Cr), lead (Pb), and also zinc (Zn). Wastewater that contain heavy metals may cause problem for waste generators because metals tend to bio accumulate and non-biodegradable. Many developing countries are now facing water pollution due to rapidly increasing of industrial and civilization (Aslam & Yousafzai, 2017).

Chromium is being used as a functional coating and as a decorative surface but it is human carcinogen and can be found in industrial effluent wastewater. Hexavalent chromium (Cr^{6+}) can be found in a large number of industrial applications because of its unique properties (Itankar & Patil, 2014). Most industries have to focus on reducing or eliminating chromium use because of its high toxicity, high cost for treatment and disposal (Imam, 2016). Therefore, there are various treatments process that can be used for the removal of heavy metal from wastewater such as chemical precipitation, coagulation, ion exchange and also adsorption by activated carbon (Gunatilake, 2015).

Adsorption process is one of the methods that is used to treat industrial effluents and able to accumulate heavy metal from heavy industrial wastewater by using activated carbon. There consists of three stages for the mechanism od adsorption at solid-liquid interface adsorption which are film diffusion, intraparticle diffusion and adsorption of the adsorbate on the exterior surface of the adsorbent. Film diffusion is a process to transport of the adsorbate from the bulk solution to the external surface of the adsorbent while intraparticle diffusion is to transport of the adsorbate within the pores of the adsorbent. Overall rate of adsorption process is determined by the slowest of these mechanism steps. Activated carbon is known as porous material that has large specific surface area to adsorb metals ions and thus several modifications have to be applied to the porous surface of activated carbon. Activated carbon is modified by being impregnated with surfactant called as Sodium Lauryl Sulfoacetate (SLSA) for enhancing the adsorption process to remove Chromium ions. SLSA is an anionic plant-based surfactant to increase the percentage removal of Chromium ions from aqueous solution. SLSA has its own critical micelle concentration (CMC) where it will be forming micelle instead of being impregnated onto the surface of activated carbon when it goes beyond this level. The objectives of this study were to study the characterization of the activated carbon before and after impregnation process and to study the efficiency of surfactant impregnated activated carbon on the adsorption of chromium ion at different impregnation ratio.

II. METHODOLOGY

A. Materials

Sodium Lauryl Sulfoacetate (SLSA) with molecular weight 330.415 $gmol^{-1}$ was supplied from Sigma-Aldric, Malaysia. While, Potassium dichromate ($K_2Cr_2O_7$) with purity of 99.8% was used as the source of Cr(VI) in synthetic wastewater and supplied from Sigma-Aldrich, Malaysia. Figure 1 and figure 2 below shows the chemical structures of the materials involved.

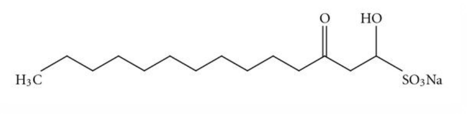

Figure 1: Sodium Lauryl Sulfoacetate (SLSA)

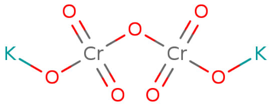

Figure 2: Potassium dichromate ($K_2Cr_2O_7$)

B. *Adsorbent*

Granular activated carbon (AC) used as an adsorbent in this study was obtained from Soon Ngai Engineering.

C. *Surfactant Impregnated Activated Carbon (SIAC)*

SLSA solution was prepared at different concentration at 10 mg/L, 25 mg/L, 50 mg/L, 75 mg/L, 100 mg/L, 125 mg/L, 150 mg/L and 175 mg/L. 2 g of AC was impregnated with SLSA at different concentrations. The conical flask was enclosed with aluminium foil and agitated in incubator shaker for 24 hours at 60ºC and 130 rpm. The solution and modified AC were filtered using Whatman filter paper and dried overnight in oven at 60ºC. The modified AC were analysed using BET analyser to determine the pore structure and surface area.

D. *Adsorption experiment*

Potassium dichromate solution was prepared by mixing of 424 mg potassium dichromate powder with 1000 mL of distilled water to obtain 130 mg/L concentration of potassium dichromate solution and was shaken continuously until it dissolved completely in water. 100 mL of potassium dichromate solution was prepared in 250 mL conical flask and 2 g of SIAC was added into the flask. The mixture was agitated in incubator shaker at 130 rpm and 30ºC for 6 hours. The mixture was filtered using Whatman filter paper and the filtered solution will be analysed using Atomic Adsorption Spectrophotometer (AAS) to determine the percentage removal of chromium.

The percentage removal (%R) of Cr(VI) is calculated as follows:

$$\%R = \frac{C_i - C_e}{C_i} \times 100$$

C_i (mg/L) is the initial concentration of Cr(VI) while C_e (mg/L) is the concentration of Cr(VI) at equilibrium.

While adsorption capacity of Cr(VI) is calculated using formula:

$$q_t = \frac{(C_i - C_t) \times V}{m}$$

q_t (mg/g) is the amount adsorbed at time t (min), C_t (mg/L) is the concentration of Cr(VI) at time t, while V (L) is the volume of Cr(VI) solution and m (g) is the mass of the adsorbent used.

E. *Analysis*

a) BET surface area and pore distribution

Brunauer-Emmett-Teller (BET) equation is used to calculate the surface area of activated carbon within pressure range 0.05-0.35.

b) Fourier transform infrared (FTIR) analysis

Fourier transform infrared (FTIR) analysis is used to determine the functional group present on the surface of SLSA in order to understand the mechanism of Cr(VI) adsorption.

c) Atomic Adsorption Spectrophotometer (AAS)

Atomic Adsorption Spectrophotometer (AAS) is used to calculate the remaining amount of Chromium that not being absorbed by AC.

III. RESULTS AND DISCUSSION

1. *Characterization of anionic surfactant*

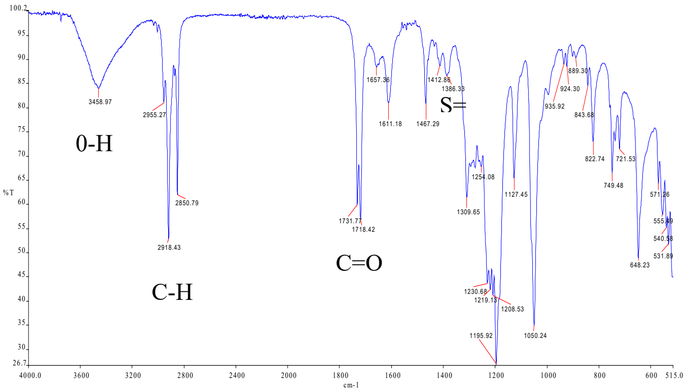

Figure 3: IR spectra of SLSA

Sodium Lauryl Sulfoacetate (SLSA) is an anionic surfactant that is used in this study as a surface modification to be impregnate on the surface of AC. Based (Ahn, Donghee, Woo, & Park, 2008), it also uses anionic surfactant to enhance the adsorption capacity of activated carbon for cadmium. This study suggests that the adsorption of cationic metal on activated carbon can be increase by the presence of anionic surfactant. SLSA has negative functional head that can attract cationic metal by electrostatic attraction and this will increase the percent removal of cationic metal that represent by sulfate functional group (S=O). Based on Fig. 3, there is a peak of C-OH at 458.97 cm^{-1} and peak of C=O 1718.42 cm^{-1}. Cr (VI) was being adsorbed onto the surface of SIAC by electrostatic attraction and ion exchange due to the negatively charged surfaces, the hydroxyl group of surfactants.

The functional group of this surfactant can be determined from the IR spectra are shown in table below.

Table 1: Functional group determined from the IR spectra.

Functional group	Adsorption (cm^{-1})
Sulfate (S=O)	1412.86, 1386.33
Phenol (O-H)	1309.65
Carboxylic acid (C=O)	1718.42
Alkane (C-H)	2918.43

2. *BET analysis of granular activated carbon (GAC)*

BET analysis was performed to calculate the total pore surface area of activated carbon. The value of total pore surface area can help to determine the correlation of mesopores and heavy metal removal capacity of AC. It can be simplified that better removal of heavy metal ions may be affected by the larger pore surface area due to availability of adsorption area.

For this study, it is expected that virgin GAC have a larger surface area compared to surfactant impregnated GAC. Impregnation of SLSA on AC will reduce the surface area of AC but it will enhance its affinity to adsorb cationic heavy metal ions.

Table 2: Volume and surface area of GAC

Pore volume, cm^3/g	0.2331
Total area in pores, m^2/g	72.582
Maximum pores volume at P/P_0, cm^2/g	0.403962
Micropores surface area, m^2/g (Dubinin-Radushkevich)	975.5684
Micropores surface area, m^2/g (Dubinin-Astakov)	1030.5798

Based on Table 2, it can be concluded that AC being used in this study has smaller surface area compared to other types adsorbent being used in industry. A study by A. Behnamfard et al. indicates that a coconut shell-based granular AC has total area in pores at 1025.03 m^2/g which is higher than total area of GAC which is at 72.582 m^2/g.
This size distribution of AC will affect for promoting the diffusion of heavy metal ions present in the solution within the internal porosity of AC. This factor will help in improving the adsorption kinetics for this study.

3. *Stability of modification*

Surfactant with higher molecular weight of hydrocarbon should be more hydrophobic and expected to have higher sorption affinity to AC (Lee, Yoon, Choe, Lee, & Choi, 2018). The surface loading efficiency on the molecular weight of hydrocarbon chain can contribute to the competitive partitioning between surfactant micelle and the AC surface. Micelle is favourable to form at higher CMC. Therefore, this contributes surfactants forming more micelle instead of being adsorbed to the AC (Asadov, et al., 2019). Hydrophobic reaction is a reaction that occur when anionic surfactant is bound to activated carbon in which hydrophobic alkyl chain of the surfactant will interact with the nonpolar portion of the activated carbon's surface (Ahn, Donghee, Woo, & Park, 2008). This hydrophobicity will determine the stability of the modification and this will determine the performance of the SIAC during operation period. Therefore, the adsorption of Cr(VI) is low at higher concentration due to the surfactant becomes micelle and not being impregnated totally to the AC.

4. *Mechanism of Cr(VI) adsorption*

a) Removal behaviors of Cr (VI) by activated carbons.

Table 3: Average percentage removal of Cr (VI) ion

Type of Activated Carbon	Average percent removal (%)
Virgin	45.76
SIAC at 10 ppm	45.65
SIAC at 25 ppm	43.99
SIAC at 50 ppm	41.00
SIAC at 75 ppm	35.81
SIAC at 100 ppm	39.46
SIAC at 125 ppm	44.34
SIAC at 150 ppm	38.80
SIAC at 175 ppm	36.53

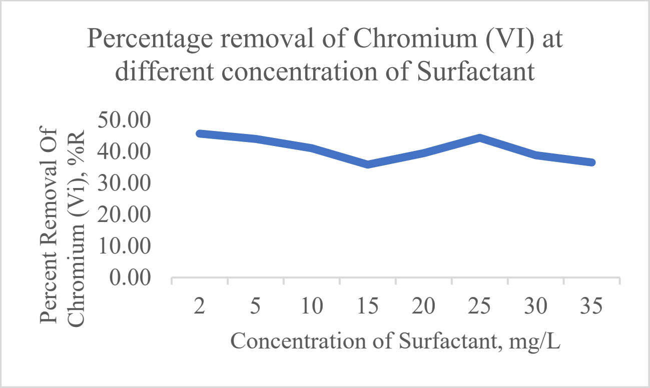

Figure 4: Percentage removal of Cr(VI) at different concentration of Surfactant.

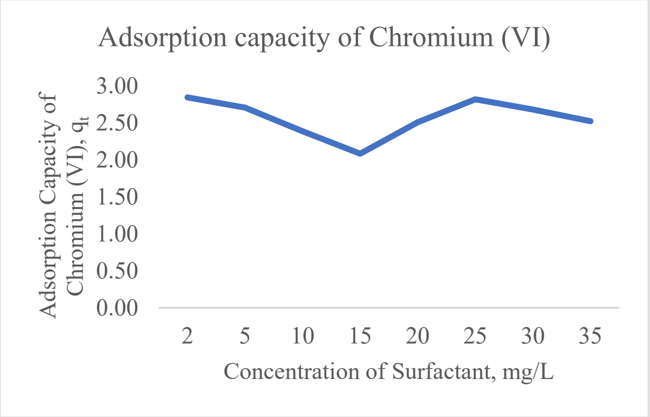

Figure 5: Adsorption capacity of Cr(VI) at different concentration of Surfactant.

$K_2Cr_2O_7 \rightarrow 2\ K^+ + Cr_2O_7^{2-}$

$Cr_2O_7^{2-} + H_2O \leftrightarrow 2\ CrO_4^{2-} + 2\ H^+$

Based on equation above, it can be concluded that hexavalent chromium is present in form of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) ions (Khezami & Capart, 2005). From potassium dichromate solution, hexavalent chromium exists as dichromate ($Cr_2O_7^{2-}$) ions where it is an anionic ion (Choi, et al., 2009). Thus, this shows that there is an electrostatic repulsion between Cr(VI) and the head group of anionic surfactants. Therefore, the higher the concentration of surfactant that being impregnated on the AC, the lower the adsorption capacity of Cr(VI) as can be seen in Fig. 5.

Originally, AC had positively charged functional groups on the surface, but after impregnation process, the surface of AC was introduced to have negative adsorption site there. The adsorption rate of Cr(VI) is higher for raw AC compare to SIAC. Based on Fig. 4, the percent removal of Cr(VI) for 2 mg of surfactant is at 45.65% compare to the percent removal of Cr(VI) for 35 mg of surfactant at 36.53%. At low concentration of surfactant, the surfactant did not fully cover the pore size of raw AC and this makes the positively charged functional group of AC attract the Cr(VI) by electrostatic interaction.

However, at high concentration of SLSA, the adsorption of chromium ions is decreasing as the impregnated SLSA has already occupy the micropores of AC and thus leaving dichromate ($Cr_2O_7^{2-}$) ions have no space to be adsorbed. As described previously, the anionic head of surfactant blocked the access of Cr(VI) to be absorbed on the AC.

b) Physisorption of chromium ion to SIAC

Coulomb forces (dipole-dipole) is a physical interaction that could lead to adsorption of heavy metal ions on the surface of activated carbon. Potassium dichromate is a polar molecule that has dipole moment and this leads to have coulomb forces for the interaction between chromium ions and SIAC (Motta, L., 2007).
Coulomb forces are weak and this causes less attraction of chromium ions onto the SIAC. This is due to chromium ions has less atomic radius and the atom is smaller. Thus, the outer electrons are closer to the nucleus and become more strongly attracted to the center. Therefore, it becomes more difficult to attract chromium ions onto the activated carbon.

c) pH adjustment

Adjustment of pH also needed to be considered. This is because the adsorption process may be affected by the possibilities of other subsidiary substances and hydrogen bonding. The pH of this study was fixed at pH 7 at all concentration of SLSA. Based on the result obtained, it shows that the adsorption of metals was not too effective at pH 7 where the percent removal of Cr(VI) almost below 50% for all samples. Based (Jyotikusum, Sahu, Sahoo, Mohanty, & Meikap, 2008) it shows that the percent adsorption of Cr(VI) decreases with increase in pH. This behaviour can be explained by considering the nature of adsorbent in metals adsorption at different pH.

The wall of activated carbon consists of large number of surface functional groups. At low pH, the degree of surface protonation is high and this makes the surface offers maximum positive charge for the adsorption of $HCrO_4^-$ and $Cr_2O_7^{2-}$ anions. As the pH increases, the degree of surface protonation will be decreased and the surface become more negatives. So, this makes the adsorption process decreases. The electrostatic repulsion occurred between the negatively charged surface of the adsorbent and negatively charged Cr(VI) ions and this reduce the removal of Cr(VI) (Leyva-Ramos, et al., 2008).

IV. CONCLUSION

Adsorption of Cr(VI) by activated carbon was modified by impregnation with anionic plant-based surfactant. This study can help to reduce the dependency of industry from using chemical based surfactant by replacing it using plant-based surfactant that is more economical and safer to the environment. Based on the result, it shows that the higher the concentration of surfactant being impregnated, the lower the adsorption of Cr(VI) ions. This study shows that electrostatic repulsion occur between the Cr(VI) ions and the SIAC as the surfactant being used was anionic surfactant. In conclusion, this shows that anionic surfactant is not effective for the removal of Cr(VI) ions as it appears as anionic ion in form of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) ions.

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